

DI ANSWER 1 OF 1 MARPAT COPYRIGHT PAGE 2 ACP

AB 1:41:14.00 MARPAT

IN 1:41:14.00

TI Rubber compositions with vibration-damping and low heat-buildup ability

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IT Patent

LA Japanese

IC ICM C08L021-00

ICS C08K005-39; C08K005-40; C08K005-57

IC 34-10 (Synthetic Elastomers and Natural Rubber)

PATENT

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DI	JP 58021675	A2	19960123	JP 1994-184238	19940704 ---
OS	MARFAT 124:234673				
AB	Title comps. contain thiurams (R1R2R3R4) 2Sx [R1, R2 = Ph, benzyl, C1-18 linear, branched, or cyclic alkyl, C3-8 alicyclic group residues or heterocyclic other than N residues; x = 1-6] 0.1-5.0, dialkyltin oxides R3R4SnO n, R3, R4 = C1-n alkyl, n = 1-6, 0.1-5.0, and/or Zn dithiocarbamates 0.1-5.0 phr. A natural rubber compn. contg. S 2, tetrastearylthiuram disulfide 2.38, and polymeric dioctyltin oxide 0.98 phr was vulcanized at 150.degree. for 10 min to form a product with a 23.degree. tan.delta. of 0.0610 and ratio of dynamic modulus at 100 Hz and 1 Hz of 1.040.				
BT	thiuram sulfide vulcanizer; dialkyltin oxide vulcanizer; zinc dithiocarbamate vulcanizer; heat buildup redn vulcanizer; vibration damper rubber vulcanizer				
IT	Sulfides, uses RL: CAT (Catalyst use); USES (Uses) mono- or poly-; rubber comps. with vibration-damping and low heat-buildup ability)				
IT	Rubber, butadiene-styrene, properties Rubber, natural, properties RL: PRP (Properties) (thiuram sulfide- and/or zinc dithiocarbamate- and/or (polymeric) dialkyltin oxide-contg. comps. with vibration-damping and low heat-buildup ability)				
IT	Vulcanization accelerators and agents (thiuram sulfide- and/or zinc dithiocarbamates and/or polymeric dialkyltin oxides for rubber comps. with vibration-damping and low heat-buildup ability)				
IT	97-74-5, Tetramethylthiuram monosulfide 97-77-8, Tetraethylthiuram disulfide 136-23-2, Zinc dibutyldithiocarbamate 137-26-8 818-03-6 1834-02-2, Tetraethylthiuram disulfide 10531-85-2, Tetrabenzyl thiuram disulfide 13878-54-1 27517-48-2 37437-21-1, Tetrakis(2-ethylhexyl)thiuram disulfide 41365-24-6 62652-50-0, Tetrahexylthiuram disulfide 70605-35-5 175079-40-0 RL: CAT (Catalyst use); USES (Uses) rubber comps. with vibration-damping and low heat-buildup ability)				
IT	9803-55-8 RL: PRP (Properties) rubber, thiuram sulfide- and/or zinc dithiocarbamate- and/or (polymeric) dialkyltin oxide-contg. comps. with vibration-damping and low heat-buildup ability)				

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## CLAIMS

[Claim(s)]

[Claim 1] As opposed to the rubber component 100 weight section [Formula 1]

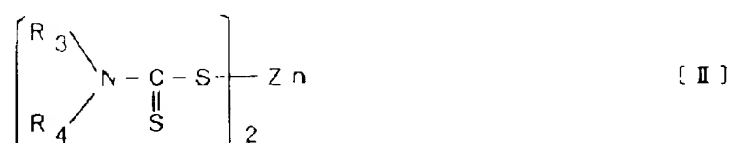
一般式



〔ただし、 $R_1$ 、 $R_2$ はそれぞれ独立して炭素数1～18の直鎖アルキル基、分岐鎖アルキル基、環状アルキル基あるいはフェニル基、ベンジル基を示し、更に $R_1$ 、 $R_2$ を連結せしめた炭素数5～8の脂環状基又は一般式〔I〕中に示されている窒素原子以外にヘテロ原子を含む複素環を示す。 $X$ は1～6の整数を示す。〕

[Formula 2]

一般式



〔ただし、 $R_3$ 、 $R_4$ はそれぞれ独立して炭素数1～18の直鎖アルキル基、分岐鎖アルキル基、環状アルキル基あるいはフェニル基、ベンジル基を示し、更に $R_3$ 、 $R_4$ を連結せしめた炭素数5～8の脂環状基又は一般式〔II〕中に示されている窒素原子以外にヘテロ原子を含む複素環を示す。〕

[Formula 3]

## 一般式



〔ただし、 $R_5$ 、 $R_6$  はそれぞれ独立して炭素数 1～8 のアルキル基を、 $n$  は 1 以上の整数を示す。〕

The rubber constituent which blends the dialkyl tin oxide 0.1 - the 5.0 weight sections which are expressed with the dithiocarbamic-acid zinc compound 0.1 - the 5.0 weight sections which are expressed with the thiuram compound 0.1 - the 5.0 weight sections, and/or the above-mentioned general formula [II] which are expressed with the above-mentioned general formula [I], and the above-mentioned general formula [III], and is characterized by the bird clapper.  
[Claim 2] As opposed to the rubber component 100 weight section [Formula 4]

## 一般式



ただし、 $R_7$ 、 $R_8$  はそれぞれ独立して炭素数 8～18 の直鎖アルキル基、分岐鎖アルキル基、環状アルキル基を示す。 $X$  は 1～6 の整数を示す。〕

The rubber constituent which blends the thiuram compound 0.1 - the 5.0 weight sections which are expressed with the above-mentioned general formula [IV], and is characterized by the bird clapper.

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention is called for short the tetrapod alkyl thiuram compound [less or equal and "the specific thiuram compound" which are a thiuram compound and/or a dithiocarbamic-acid zinc compound, dialkyl tin oxide, or the specific thiuram compound 8-18, i.e., the carbon numbers of an alkyl group, in more detail about a rubber constituent. ] By \*\*\*\*\* (ing), \*\*\*\*\* is reduced and it is related with the rubber constituent and low febrility rubber constituent which have the outstanding damping characteristic

[0002]

[Description of the Prior Art] Various material is used in order to absorb or reduce various kinds of vibration or noise generated from an automobile, an industrial machine, etc., about a rubber vibration insulator. For example, since it is necessary to have the endurance which reduces vibration or noise of an engine, the power transfer section, axle part, etc., and can support each part article as a rubber vibration insulator for automobiles, natural rubber, styrene-butadiene rubber (SBR), butadiene rubber (BR), or those blend rubber is mainly used.

[0003] In order to reduce vibration or noise, it is required to make small \*\*\*\*\* which is the property of a rubber vibration insulator, and to enlarge a 10-30Hz loss factor (tandelta). By considering as liquid enclosure mounting as a vibroisolating material, adjustment of tandelta is being attained very broadly.

[0004] However, \*\*\*\*\* is influenced by the physical properties of a rubber vibration insulator. That is, although technique, such as reduction of the loadings of the carbon black which is the increase in sulphuric loadings, the use of butadiene rubber, or the reinforcing agent whose low \*\*\*\*\*-ization of a rubber vibration insulator is a vulcanizing agent, is adopted, use of butadiene rubber or low restoration of carbon black reduces the endurance of rubber goods with the heat-resistant fall of the rubber goods from which sulphuric increase in quantity is obtained

[0005] Furthermore, although improvement of the rubber vibration insulator property by addition of a dinitro diamine compound is indicated by JP.1-254747.A and JP.1-315441.A, this written compound has the fault of reducing the processing stability of an unvulcanized rubber remarkably. The present condition is that difficult \*\* of a raise in the life of the latest autoparts and the request to the ease of processing is carried out by the technique indicated conventionally [ above-mentioned ] at the chip box which is becoming still severer, and sufficient purpose achievement

[0006] On the other hand, since it corresponds to the social demand of saving resources and energy saving about a low febrility rubber constituent, in the rubber industry, especially the tire industry, development of a low mpg tire is briskly performed over the past several years, and a low febrility rubber constituent is then indispensable. For example, although there was the method of using the styrene-butadiene rubber which controlled the content of a combined styrene and vinyl combination as especially indicated by JP.57-51503.A, JP.57-55204.A, and JP.58-36705.A for the purpose of the tire for passenger cars, these methods were inapplicable to rubber other than SBR, especially the natural rubber currently most widely used for the tire for heavy vehicles at all

[0007] Furthermore, it is indicated by by adding oximido quinolines to JP.50-38131.B, the British patent No. 1185896, U.S. Pat. No. 2315855, and patent No. 2315856 that the febrility of a rubber constituent is improved. However, although surely such a nitroso compound has improved febrility, when it applied to especially polyisoprene rubber, it had the fault that a \*\*\*\*\* operation of polymer reduced the abrasion resistance of a rubber constituent remarkably greatly. Moreover, although the above-mentioned nitroso compound improves febrility remarkably when it applies to polyisoprene rubber, when it applies to synthetic rubber, for example, styrene-butadiene rubber, butadiene rubber, etc., the present condition is that the febrile improvement effect was seldom expectable

[0008]

[Problem(s) to be Solved by the Invention] It is providing the field with the rubber constituent which has little influence to the processing stability and the vulcanized-rubber physical properties of an unvulcanized rubber, and may raise a rubber vibration insulator property using an added type medicine with easy processability to the rubber constituent which has the outstanding damping characteristic. On the other hand, the problem which a plain-gauze \*\*\*\* operation can be large about a low febrility rubber constituent when it applies to above natural rubber and above polyisoprene rubber, or can seldom expect the exoergic improvement effect when it applies to styrene-butadiene rubber further tends to be solved, and it is going to offer a low febrility rubber constituent without such a fault

[0009]

[Means for Solving the Problem] This invention persons receive the rubber component 100 weight section, as a result of inquiring wholeheartedly in view of the above-mentioned trouble. [0010]

[Formula 5]

一般式



〔ただし、 $R_1$ 、 $R_2$ はそれぞれ独立して炭素数1～18の直鎖アルキル基、分岐鎖アルキル基、環状アルキル基あるいはフェニル基、ベンジル基を示し、更に $R_1$ 、 $R_2$ を連結せしめた炭素数5～8の脂環状基又は一般式〔I〕中に示されている窒素原子以外にヘテロ原子を含む複素環を示す。 $X$ は1～6の整数を示す。〕

[0011]

[Formula 6]

一般式



〔ただし、 $R_3$ 、 $R_4$ はそれぞれ独立して炭素数1～18の直鎖アルキル基、分岐鎖アルキル基、環状アルキル基あるいはフェニル基、ベンジル基を示し、更に $R_3$ 、 $R_4$ を連結せしめた炭素数5～8の脂環状基又は一般式〔II〕中に示されている窒素原子以外にヘテロ原子を含む複素環を示す。〕

[0012]

[Formula 7]

一般式



〔ただし、 $R_5$ 、 $R_6$ はそれぞれ独立して炭素数1～8のアルキル基を、 $n$ は1以上の整数を示す。〕

[0013] the chalky tin oxide 0.1 - the 5.0 weight sections which are expressed with the dithiocarbamic-acid zinc compound 0.1 - the 5.0 weight sections which are expressed with the thiram compound 0.1 - the 5.0 weight sections, and/or the above-mentioned general formula [II] which are expressed with the above-mentioned general formula [I], and the above-mentioned general formula [III] -- or -- [0014]

[Formula 8]  
一般式



ただし、 $\text{R}_7$ 、 $\text{R}_8$  はそれぞれ独立して炭素数 8～18 の直鎖アルキル基、  
分岐鎖アルキル基、環状アルキル基を示す。 $X$  は 1～6 の整数を示す。]

[0015] When the specific thiuram compound 0.1 - the 5.0 weight sections which are expressed with the above-mentioned general formula [IV] are blended, for it to be surprised about a rubber vibration insulator constituent The rubber vibration insulator property of the vulcanized-rubber constituent, especially decline in \*\*\*\*\* are found out, about a low febrility rubber constituent The exoergic improvement effect that it is high when the high exoergic improvement effect applies to styrene-butadiene rubber further is found out without doing a \*\*\*\*\* operation, when it applies to natural rubber and polyisoprene rubber, and it came to complete this invention based on these knowledge

[0016] The thiuram compound and/or the dithiocarbamic-acid zinc compound, the above-mentioned dialkyl tin oxide, or the above-mentioned specific thiuram compound of this invention is easily added during rubber processing to the constituent for rubber vibration insulators. The feature has little influence and it may raise a rubber vibration insulator property to the processing stability and the vulcanized-rubber physical properties of an unvulcanized rubber Furthermore, there is little influence of the processing stability on an unvulcanized rubber to a low febrility rubber constituent. And it has the feature which it not only demonstrates the low febrility improvement effect, but can demonstrate the low febrility improvement effect to styrene-butadiene rubber etc., without carrying out and doing a 8 solution operation, when it applies to natural rubber and polyisoprene rubber.

[0017] As rubber which makes the subject of the rubber constituent of this invention Polyisoprene rubber (IR) besides natural rubber, styrene-butadiene rubber (SBR), Although various synthetic rubber, such as butadiene rubber (BR), acrylonitrile-butadiene rubber (NBR), isobutylene isoprene rubber (IIR), chloroprene rubber (CR), and ethylene-propylene rubber (EPDM), is illustrated About the constituent for rubber vibration insulators, one or more sorts of blend rubber of the above-mentioned synthetic rubber which made natural rubber or natural rubber the subject further from points, such as vibration isolation nature, about a low febrility rubber constituent It is natural rubber, polyisoprene rubber, styrene-butadiene rubber, butadiene rubber, isobutylene isoprene rubber, etc., and independent or two or more sort combined use is preferably used in these rubber

[0018] The thiuram compound of the above-mentioned general formula [I] concerning this invention Tetramethylthiurammonosulfide, tetramethylthiuramdisulfide, A tetraethylthiuram disulfide, tetrabutylthiuram disulfide, Tetrapod hexyl thiuram disulfide, tetrapod benzyl thiuram disulfide, Screw (N-ethyl-N-phenyl) thiuram disulfide, tetrakis (2-ethylhexyl) thiuram disulfide, Although tetrapod stearyl thiuram disulfide, dipentamethylenethiuramtetrasulfide, a JIPENTAMECHIREN thiuram hexa sulfide, tetraacelo hexyl thiuram disulfide, and dimorpholino thiuram disulfide are mentioned It is not limited to these

[0019] The dithiocarbamic-acid zinc compound of the above-mentioned general formula [II] concerning this invention A zinc dimethyldithiocarbamate, a zinc diethyldithiocarbamate, Zinc dibutyldithiocarbamate, N-ethyl-N-phenyl dithiocarbamic-acid zinc, N-pentamethylene dithiocarbamic-acid zinc, dibenzyl dithiocarbamic-acid zinc, Although screw (2-ethylhexyl) dithiocarbamic-acid zinc, dihexyl dithiocarbamic-acid zinc, distearyl dithiocarbamic-acid zinc, dicyclohexyl dithiocarbamic-acid zinc, and morpholino dithiocarbamic-acid zinc are mentioned, it is not limited to these An above-mentioned thiuram compound and an above-mentioned dithiocarbamic-acid zinc compound can be adjusted by the well-known method.

[0020] A monomer type ( $n=1$ ) or polymer types ( $n \geq 2$ ), such as dimethyl tin oxide, di-n-butyl tin oxide, and G n-oetyl tin oxide, are mentioned, and, as for the dialkyl tin oxide of the above-mentioned general formula [III] concerning this invention, especially the monomer type or polymer type of di-n-butyl tin oxide and G n-oetyl tin oxide has commercial usable elegance. The specific thiuram compound of the above-mentioned general formula [IV] concerning this invention is not limited to these, although tetrakis (2-ethylhexyl) thiuram disulfide and tetrapod stearyl thiuram disulfide are mentioned. This kind of specific thiuram compound can also be adjusted by the well-known method

[0021] The loadings to the rubber 100 weight section of the above-mentioned thiuram compound concerning this invention and a dithiocarbamic-acid zinc compound are the 0.1 - 5.0 weight section, and in order that vulcanization speed may become quick in the amount which there are almost no target vibrationproofing effect and target exoergic improvement effect, and exceeds the loadings and they may worsen the processing stability of an unvulcanized-rubber constituent remarkably, they are difficult to use it at under the loadings However, the vibrationproofing effect and especially the exoergic improvement effect are demonstrated by the combined use with specific thiuram compound independent use or a thiuram compound and/or a dithiocarbamic-acid zinc

compound, and dialkyl tin oxide

[0022] The loadings to the rubber 100 weight section of the above-mentioned specific thiuram compound concerning this invention are the 0.1 - 5.0 weight section, and in order that vulcanization speed may become quick in the amount which there are almost no target vibrationproofing effect and target exoergic improvement effect, and exceeds the loadings and they may worsen the processing stability of an unvulcanized-rubber constituent remarkably, they are difficult to use it at under the loadings. The loadings to the rubber 100 weight section of the dialkyl tin oxide concerning this invention are the 0.1 - 5.0 weight section, in the amount which there are almost no target vibrationproofing effect and target exoergic improvement effect, and exceeds the loadings, they make vulcanization speed late and it becomes difficult to vulcanization speed adjust them under at the loadings

[0023] The above-mentioned thiuram compound (a specific thiuram compound is also included) and above-mentioned dithiocarbamic-acid/zinc compound concerning this invention are usually used as the vulcanization accelerator for rubber, or agricultural chemicals although it is an example, what tetrakis (2-ethylhexyl) thiuram disulfide has an effect for as a vulcanization accelerator for rubber is reported to [Society of Rubber Industry, Japan, the 45th volume octavus number, and 745 (1972)] However, the indication about improving the damping characteristic of a rubber constituent and febrility is not yet found out like this invention by adding these thiuram compounds and/or a dithiocarbamic-acid zinc compound, dialkyl tin oxide, or a specific thiuram compound

[0024] Although what has been used conventionally can use the compounding agent blended with the rubber constituent concerning this invention as it is When it illustrates, metallic oxides, such as fatty acids, such as stearin acid, a zinc oxide, and a magnesium oxide, Vulcanizing agents, such as sulfur, a thiazole system, a sulfenamide system, a thiuram system, Vulcanization accelerators, such as a dithiocarbamic-acid salt system and a thiourea system, an amine system, Antioxidants, such as a phenol system, an imidazole system and a dithiocarbamic-acid metal salt, and a wax, It shall also be included by the claim of this invention that compounding agents for rubber, such as a bulking agent of softeners, such as straight mineral oil, carbon black, and an inorganic system, a reinforcing agent, and a tackifier, may be suitably blended according to the purpose. It is a book below.

[0025]

[Example]

Based on combination of examples 1-15, the example 1 of comparison - 10, table 1, the thiuram compound or dithiocarbamic-acid/zinc compound based on the loadings of rubber, a zinc oxide, stearin acid, carbon black, and Table 2 by 75 cc Banbury mixer [Oriental Energy Machine factory lab plastic strike mill], dialkyl tin oxide, or the thiuram compound (a specific thiuram compound is included) was kneaded for 4 minutes with the rotational speed of 70rpm. The rubber temperature at the time of the milling going up was 140-150 degrees C. Subsequently, based on Table 1, a vulcanization accelerator and sulfur are kneaded for this kneading object with the test roll of 50-60 degrees C of roll skin temperatures, and it is JIS about this unvulcanized-rubber constituent after that. K Based on 6300-1994 (the unvulcanized-rubber physical-test method die vulcanization examination A method), the curelast meter examination [150 degrees C, amplitude angle: \*\*3 degree] was performed. Furthermore, press cure is carried out on the vulcanization conditions which show this unvulcanized-rubber constituent in Table 2, a vulcanized-rubber constituent is produced, this vulcanized-rubber constituent is used, and it is JIS. Ordinary state physical properties are measured based on K6301 (the vulcanized-rubber physical-test method), and it is JISK further. Based on 6254 (the stress and strain test method in low deformation of vulcanized rubber), the static modulus (G25) was measured at 23 degrees C. Furthermore, a dynamic modulus (E') and tandelta were measured at 23 degrees C by Oriental Energy Machine factory LEO log rough solid. However, \*\*\*\*\* was computed by  $(100 \text{ Hz } E') / (1 \text{ Hz } E')$ . Those results were shown in Table 2

[0026]

[Table 1]

表

1

天然ゴム	100
酸化亜鉛	5
ステアリン酸	1
FEFカーボンブラック	40
硫黄	2
加硫促進剤 (*1) ノクセラーCZ	1
供試試料	[表2に記載]

\*1) ノクセラーCZ : N-シクロヘキシル-2-

ベンゾチアゾリルスルフェンアミドの大内新興

化学工業株式会社商品名。

[0027]

[Table 2]

表 2 (その1)

		実 施 例										
		1	2	3	4	5	6	7	8	9	10	
供試 試料	*2) TR・DC	*4) TST	*5) TOT	*6) THY	*7) TBT	*8) YET	*9) TT	*10) TS	*11) TBZT	*12) TPET	*13) BZ	
	配合量 [PHR]	2.38	1.28	1.04	0.82	0.21	0.17	0.15	1.09	0.78	0.95	
	*3) 銅化合物	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	
	配合量 [PHR]	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
キュラスト メータ試験 (150℃)	t'c(10) [min]	2.3	3.4	3.2	3.2	2.5	2.0	2.6	2.3	4.0	2.0	
加硫時間 [min] 150℃		10	10	10	15	10	10	10	10	10	10	
引張試験 (常温特性)	M200[MPa]	9.9	10.4	11.1	9.9	11.9	11.8	10.5	11.5	11.5	10.6	
防振特性	G25 [MPa]	1.31	1.27	1.30	1.26	1.41	1.40	1.35	1.36	1.38	1.28	
	動係率	1.040	1.045	1.065	1.063	1.054	1.050	1.052	1.059	1.047	1.060	
	tan δ [20Hz]	0.0610	0.0685	0.0677	0.0699	0.0720	0.0659	0.0689	0.0758	0.0758	0.0688	
	100Hz [MPa]	3.854	3.955	4.173	3.583	3.745	4.306	4.345	4.308	4.338	4.320	
	1Hz [MPa]	3.706	3.785	3.918	3.371	3.554	4.101	4.130	4.068	4.142	4.076	

\*2) TR・DC : チウラム化合物 (特定チウラム化合物を含む。) 及びジチオカルバミン酸亜鉛化合物。

\*3) 銅化合物 : BT0 (P) ; ジブチル銅オキシド (ポリマータイプ) , BT0 (H) ; ジブチル銅オキシド (モノマータイプ) ,

DT0 (P) ; ジオクチル銅オキシド (ポリマータイプ)



表 2 (その2)

		実 例					比 較 例				
		11	12	13	14	15	1	2	3	4	5
供試 試料	*2) TR・DC	*14) ZP	*5) TOT	*5) TOT	*4) TST	*5) TOT	*6) THT	*7) TBT	*8) TET	*9) TT	*10) TS
	配合量 [PHR]	1.22	1.26	1.20	2.38	1.26	1.04	0.82	0.21	0.17	0.15
	*3) 銅化合物	BTO (P)	BTO (M)	OTO (P)	—	—	—	—	—	—	—
	配合量 [PHR]	0.99	0.99	0.99	—	—	—	—	—	—	—
キュラスト メータ試験 (150℃)	t'c(10) [min]	1.7	3.5	3.9	2.3	2.9	2.7	2.3	2.2	1.8	2.8
加硫時間 [min] 150℃		10	10	10	10	10	10	10	10	10	10
引張試験 (常態物性) M200 [MPa]		10.3	10.5	11.3	10.6	12.3	12.5	13.3	12.5	12.9	12.7
防振特性	G25 [MPa]	1.34	1.29	1.32	1.32	1.38	1.49	1.50	1.48	1.59	1.58
	動倍率	1.050	1.045	1.053	1.045	1.048	1.076	1.074	1.068	1.063	1.078
	$\tan \delta$ [20Hz]	0.0577	0.0691	0.0703	0.0694	0.0723	0.0709	0.0678	0.0673	0.0527	0.0768
	100Hz [MPa]	3.953	3.980	4.103	4.178	4.454	4.664	4.763	4.653	4.544	5.070
	1Hz [MPa]	3.765	3.786	3.900	3.998	4.252	4.333	4.436	4.356	4.276	5.017

表 2 (その3)

		比較例				
		6	7	8	9	10
供試 試料	•2) TR・DC	•11)TBzT	•12)IPtI	•13) BZ	•14) ZP	—
	配合量 [PHR]	1.09	0.78	0.95	1.22	—
	•3) 銅化合物	—	—	—	—	—
	配合量 [PHR]	—	—	—	—	—
キュラスト メータ試験 (150℃)	t'c(10) [min]	1.8	3.6	2.1	1.6	4.3
加硫時間 [min] 150℃		10	10	10	10	15
引張試験 (常態物性)	M200[MPa]	12.9	11.8	12.6	12.6	12.9
防振特性	G25 [MPa]	1.59	1.49	1.52	1.54	1.43
	動倍率	1.063	1.079	1.072	1.060	1.074
	$\tan \delta$ [20Hz]	0.0527	0.0780	0.0725	0.0610	0.0741
	100Hz [MPa]	4.544	4.944	4.796	4.884	4.814
	1Hz [MPa]	4.276	4.581	4.475	4.609	4.482

- \*4) IS1 : テトラステアリルチウラムジスルフィド \*5) TOT : テンキス (2-エチルヘキシル) チウラムジスルフィド  
 \*6) THT : テトラヘキシルチウラムジスルフィド \*7) TBT : テトラブチルチウラムジスルフィド  
 \*8) TET : テトラエチルチウラムジスルフィド \*9) TT : テトラメチルチウラムジスルフィド  
 \*10) TS : テトラメチルチウラムモノスルフィド \*11) TBzT : テトラベンジルチウラムジスルフィド  
 \*12) IPtI : ビス (N-エチル-N-フェニル) チウラムジスルフィド \*13) BZ : ジブチルジチオカルバミン酸亜鉛  
 \*14) ZP : N-ペンタメチレンジチオカルバミン酸亜鉛

[0028]

[Effect] Although influence is somewhat accepted in the processing stability (scorching-proof nature), vulcanization speed, and vulcanizate nature of \*\* unvulcanized-rubber constituent from the result of Table 2, from it, as for the effect of the thiuram compound or dithiocarbamic-acid/zinc compound concerning A, this invention, and dialkyl tin oxide, improvement in the vibrationproofing effect by decline in \*\*\*\*\* is accepted clearly.

B. Although influence is somewhat accepted in the processing stability (scorching-proof nature), vulcanization speed, and vulcanizate nature of \*\* unvulcanized-rubber constituent, as for the effect of the specific thiuram compound concerning this invention, improvement in the vibrationproofing effect by decline in \*\*\*\*\* is accepted clearly.

it is thought that selection of the above the thiuram compound or dithiocarbamic-acid/zinc compound concerning an effect shell and this invention, dialkyl tin oxide, or specific thiuram compound is suitably attained by the processing stability (scorching-proof nature), the vulcanization speed, and the ordinary state physical properties of the rubber vibration insulator constituent made into the purpose, and it suits the ease of processing, and it waits for it, and it is useful for the rubber industry.

[0029]

[Example]

Based on combination of examples 16-19, the example 11 of comparison - 13, table 3, the thiuram compound, the dibutyl tin oxide (polymer type), or the thiuram compound (a specific thiuram compound is included) based on the loadings of rubber, a zinc oxide, stearin acid, carbon black, and Table 4 by 75 cc Banbury mixer [Oriental Energy Machine factory lab plastic strike mill]

was kneaded for 4 minutes with the rotational speed of 70rpm. The rubber temperature at the time of the milling going up was 140-150 degrees C. Subsequently, based on Table 4, a vulcanization accelerator and sulfur, or a vulcanizing agent is kneaded for this kneading object with the test roll of 50-60 degrees C of roll skin temperatures, and it is JIS about this unvulcanized-rubber constituent after that. K Based on 6300-1994 (the unvulcanized-rubber physical-test method die vulcanization examination A method), the curelast meter examination [150 degrees C, amplitude angle \*\*3 degree] was performed. Furthermore, press cure is carried out on the vulcanization conditions which show this unvulcanized-rubber constituent in Table 4, a vulcanized-rubber constituent is produced, this vulcanized-rubber constituent is used, and it is JIS. Ordinary state physical properties are measured based on K6301 (the vulcanized-rubber physical-test method), and it is JIS further. K Based on 6254 (the stress and strain test method in low deformation of vulcanized rubber), the static modulus (G25) was measured at 23 degrees C. Furthermore, a dynamic modulus (E') and tandelta were measured at 23 degrees C by Oriental Energy Machine factory LHO log rough solid. However, the dynamic modulus was computed by  $(100\text{Hz } E')/(1\text{Hz } E')$ . Those results were shown in Table 4.

[0030]

[Table 3]

表

3

天然ゴム	100
酸化亜鉛	5
ステアリン酸	1
FEFカーボンブラック	40
硫黄又は加硫剤 (*15) バルノック R	[表4に記載]
加硫促進剤 (*1) ノクセラ-CZ	[表4に記載]
供試試料	[表4に記載]

\*1) ノクセラ-CZ : N-シクロヘキシル-2-

ベンゾチアゾリルスルフェンアミドの大内新興

化学工業株式会社商品名。

\*15) バルノック R : ジチオビスモルホリンの大内

新興化学工業株式会社商品名。

[0031]

[Table 4]

表 4

		実 施 例				比 較 例			
		16	17	18	19	11	12	13	
加 硫 用 薬 剤	*1) ノクセラ CZ	2.0	2.0	2.0	2.0	2.0	2.0	3.5	
	硫黄	0.5	0.5	—	—	0.5	—	0.5	
	*15)バルノック R	—	—	2.0	2.0	—	2.0	—	
供 試 試 料	*2) TR	*5) TOT	*5) TOT	*5) TOT	*5) TOT	*9) TT	*9) TT	—	
	配合量 [PHR]	1.5	1.5	1.5	1.5	1.0	1.0	—	
	*3) 銅化合物	BT0 (P)	—	BT0 (P)	—	—	—	—	
	配合量 [PHR]	1.0	—	1.0	—	—	—	—	
キュフスト メータ試験 (150℃)	t'C(10) [min]	5.7	5.5	8.0	7.8	4.0	6.5	7.8	
加硫時間 [min] 150℃		20	20	25	25	20	25	25	
引張試験 (常温物性)		M200 [MPa]	9.8	11.0	10.1	11.2	11.5	12.4	10.0
防 震 特 性	G25 [MPa]	1.21	1.22	1.20	1.24	1.28	1.37	1.11	
	動倍率	1.047	1.053	1.062	1.075	1.071	1.091	1.131	
	$\tan\delta$ [20Hz]	0.0672	0.0781	0.1011	0.1002	0.0992	0.1054	0.0888	
	100Hz [MPa]	4.498	4.521	4.289	4.481	4.549	4.561	4.826	
	1Hz [MPa]	4.296	4.293	4.031	4.168	4.247	4.189	4.267	

\*1) ノクセラ CZ : N-シクロヘキシル-2-ベンゾチアゾリルスルホニウムの大内新興化学工業株式会社商品名

\*2) TR : チウラム化合物 (特定チウラム化合物を含む。) \*5) TOT : テトラキス (2-エチルヘキシル) チウラムジスルフィド

\*3) 銅化合物 : BT0 (P) : ジブチル銅オキサイド (ポリマータイプ) \*9) TT : テトラメチルチウラムジスルフィド

\*15) バルノック R : ジチオビスモルホリンの大内新興化学工業株式会社商品名

[0032]

[Effect] Although influence is somewhat accepted in the processing stability (scorching-proof nature), vulcanization speed, and vulcanizate nature of \*\* unvulcanized-rubber constituent from the result of Table 4, from it, as for the effect of the thiuram compound concerning A, this invention, and dibutyl tin oxide (polymer type), improvement in the vibrationproofing effect by decline in \*\*\*\*\* is accepted clearly.

B. Although influence is somewhat accepted in the processing stability (scorching-proof nature), vulcanization speed, and vulcanizate nature of \*\* unvulcanized-rubber constituent, as for the effect of the specific thiuram compound concerning this invention, improvement in the vibrationproofing effect by decline in \*\*\*\*\* is accepted clearly.

it is thought that selection of the above thiuram compound, dibutyl tin oxide (polymer type), or specific thiuram compound concerning an effect shell and this invention is suitably attained by the processing stability (scorching-proof nature), the vulcanization speed, and the ordinary state physical properties of the rubber vibration insulator constituent made into the purpose, and it suits the ease of processing, and it waits for it, and it is useful for the rubber industry.

[0033]

[Example]

Based on combination of examples 20-24, the example 14 of comparison - 16, table 5, a thiuram compound, dibutyl tin oxide (polymer type), or a thiuram compound based on the loadings of rubber, stearic acid, carbon black, and Table 6 by 600 cc Banbury mixer [Oriental Energy Machine factory lab plastic strike mill] was kneaded for 4 minutes with the rotational speed of 70rpm (a specific thiuram compound is included). The rubber temperature at the time of the milling going up was 150-160 degrees C. Subsequently, based on Table 5, a zinc oxide, a vulcanization accelerator, and sulfur were kneaded for 10 seconds per minute by 70rpm by the above-mentioned Banbury mixer, and sheeting of this kneading object was carried out with a test roll. It is JIS about this unvulcanized-rubber constituent after that. K Based on 6300-1994 (the unvulcanized-rubber physical-test method die vulcanization examination A method), the curelax meter examination [150 degrees C, amplitude angle: \*\*3 degree] was performed. Furthermore, while measuring sol molecular weight about this unvulcanized-rubber constituent based on the following method, press cure was carried out on the vulcanization conditions shown in Table 6, the vulcanized-rubber constituent was produced, and tandelita was measured at 60 degrees C by Oriental Energy Machine factory LEO log rough solid using this vulcanized-rubber constituent. Those results were shown in Table 6.

The measuring method of sol molecular weight. It is High made from Oriental Soda at the residual liquor which was immersed in the tetrahydrofuran in the unvulcanized-rubber constituent, and removed carbon gel 48 hours after. Speed Liquid Chromatograph HLC-802A is used and it is a part for a sol. の分子量 (Mw) を測定した。

[0034]

[Table 5]

表

5

天然ゴム	100
酸化亜鉛	5
ステアリン酸	2
[SAFカーボンブラック	50
硫黄	2.5
加硫促進剤 (*16)ノクセラ-NS)	0.5
供試試料	[表6に記載]

\*16)ノクセラ-NS : N-tert-ブチル-2-ベンゾ

チアゾリルスルフェンアミドの大内新興化学

工業株式会社商品名。

[0035]

[Table 6]

表 6

		実 施 例					比 較 例		
		20	21	22	23	24	14	15	16
供試 試料	*2) TR又は*17)NHQ	*4) ISI	*5) TOT	*6) THI	*4) ISI	*5) TOT	*9) TT	*17) NHQ	—
	配合量 [PHR]	2.6	1.4	1.2	2.6	1.4	0.27	0.77	—
	*3) 銅化合物	BT0 (P)	BT0 (P)	BT0 (P)	—	—	—	—	—
	配合量 [PHR]	2.0	2.0	2.0	—	—	—	—	—
キュラスト メータ試験 (150℃)	t'c(10) [min]	4.0	4.5	4.4	3.9	4.3	3.5	4.5	5.8
加硫時間 [min] 150℃		15	15	15	15	15	15	25	30
*18) tanδ (最高値)		0.118	0.120	0.123	0.131	0.132	0.151	0.119	0.153
ゾル分子重 [Mw × 10 <sup>5</sup> ]		5.49	5.55	5.53	5.50	5.54	5.53	4.02	5.53

\*2) TR : チウラム化合物 (特定チウラム化合物を含む。) \*3) 銅化合物 : BT0 (P) ; ジブチル銅オキシド (ポリマータイプ)

\*4) TST : テトラステアリルチウラムジスルフィド \*5) TOT : テトラキス (2-エチルヘキシル) チウラムジスルフィド

\*6) THI : テトラヘキシルチウラムジスルフィド \*17) NHQ : 5-ニトロソ-8-ヒドロキシキノリン

\*9) TT : テトラメチルチウラムジスルフィド \*18) : 振幅1~7%での最高値

[0036]

[Effect] From the result of Table 6, it is distinct that there is no \*\*\*\*\* operation of polymer as contrasted with the example of comparison which the unvulcanized-rubber constituent of this invention does not have the influence to processing stability (scorching-proof nature), and blended NHQ or TT, and febrility is improved remarkably.

[0037]

[Example]

Based on combination of examples 25-26, the example 17 of comparison - 19, table 7, a thiuram compound, dibutyl tin oxide (polymer type), or a thiuram compound based on the loadings of rubber, stearin acid, carbon black, and Table 8 by 600 cc Banbury mixer [Oriental Energy Machine factory lab plastic strike mill] was kneaded for 4 minutes with the rotational speed of 70rpm (a specific thiuram compound is included). The rubber temperature at the time of the milling going up was 150-160 degrees C. Subsequently, based on Table 7, a zinc oxide, a vulcanization accelerator, and sulfur were kneaded for 10 seconds per minute by 70rpm by the above-mentioned Banbury mixer, and sheeting of this kneading object was carried out with a test roll. It is IIS about this unvulcanized-rubber constituent after that. K Based on 6300-1994 (the unvulcanized-rubber physical-test method die vulcanization examination A method), the curelast meter examination [150 degrees C, amplitude angle \*\*\*3 degree] was performed. Furthermore, while measuring sol molecular weight about this unvulcanized-rubber constituent based on the following method, press cure was carried out on the vulcanization conditions shown in Table 8, the vulcanized-rubber constituent was produced, and tandelta was measured at 60 degrees C by Oriental Energy Machine factory LEO log rough solid using this

vulcanized-rubber constituent Those results were shown in Table 8

[0038]

[Table 7]

表

7

SBR (1502)	100
酸化亜鉛	5
ステアリン酸	1
HAFカーボンブラック	40
硫黄	2
加硫促進剤 (*1) ノクセラーCZ)	1
供試試料	[表8に記載]

\*1) ノクセラーCZ : N-シクロヘキシル-2-

ベンゾチアゾリルスルフェンアミドの大内新興

化学工業株式会社商品名。

[0039]

[Table 8]

表 8

		実 施 例		比 較 例		
		25	26	17	18	19
供試 試料	*2) TR又は*17)NHQ 配合量 [PHR]	*5) TOT 1.4	*5) TOT 1.4	*9) TT 0.27	*17) NHQ 0.77	—
	*3) 銅化合物 配合量 [PHR]	BT0 (P) 2.0	—	—	—	—
	キュラスト メータ試験 (150℃)	t'c(10) [min] 7.8	7.6	6.5	8.2	8.9
加硫時間 [min] 150℃		20	20	15	20	20
*18) tan δ (最高値)		0.130	0.138	0.151	0.144	0.155

\*2) TR : チウラム化合物 (特定チウラム化合物を含む。) \*3) 銅化合物 : BT0 (P) ; ジブチル銅オキシド (ポリマータイプ)

\*5) TOT : テトラキス (2-エチルヘキシル) チウラムジスルフィド

\*9) TT : テトラメチルチウラムジスルフィド \*17) NHQ : 5-ニトロソ-8-ヒドロキシキノリン

\*18) : 振幅1~7%での最高値

[0040]

[Effect] The styrene-butadiene rubber constituent of this invention has little influence to the processing stability (scorching-proof nature) of an unvulcanized-rubber constituent, and the result of Table 8 shows that the \*\*\*\*\* operation of the exoergic improvement effect and polymer is also improved as contrasted with the example of comparison which blended NHQ or TT

[Translation done.]

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EFFECT OF THE INVENTION

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[Effect] Although influence is somewhat accepted in the processing stability (scorching-proof nature), vulcanization speed, and vulcanizate nature of \*\* unvulcanized-rubber constituent from the result of Table 2, from it, as for the effect of the thiuram compound or dithiocarbamic-acid/zinc compound concerning A, this invention, and dialkyl tin oxide, improvement in the vibrationproofing effect by decline in \*\*\*\*\* is accepted clearly.

B Although influence is somewhat accepted in the processing stability (scorching-proof nature), vulcanization speed, and vulcanizate nature of \*\* unvulcanized-rubber constituent, as for the effect of the specific thiuram compound concerning this invention, improvement in the vibrationproofing effect by decline in \*\*\*\*\* is accepted clearly.  
it is thought that selection of the above the thiuram compound or dithiocarbamic-acid zinc compound concerning an effect shell and this invention, dialkyl tin oxide, or specific thiuram compound is suitably attained by the processing stability (scorching-proof nature), the vulcanization speed, and the ordinary state physical properties of the rubber vibration insulator constituent made into the purpose, and it suits the ease of processing, and it waits for it, and it is useful for the rubber industry.

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TECHNICAL PROBLEM

[Problems to be Solved by the Invention] It is providing the field with the rubber constituent which has little influence to the processing stability and the vulcanized-rubber physical properties of an unvulcanized rubber, and may raise a rubber vibration insulator property using an added type medicine with easy processability to the rubber constituent which has the outstanding damping characteristic. On the other hand, the problem which a plain-gauze \*\*\*\* operation can be large about a low febrility rubber constituent when it applies to above natural rubber and above polyisoprene rubber, or can seldom expect the exoergic improvement effect when it applies to styrene-butadiene rubber further tends to be solved, and it is going to offer a low febrility rubber constituent without such a fault.

{0009}

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## MEANS

[Means for Solving the Problem] This invention persons receive the rubber component 100 weight section, as a result of inquiring wholeheartedly in view of the above-mentioned trouble. [0010]

[Formula 5]

一般式

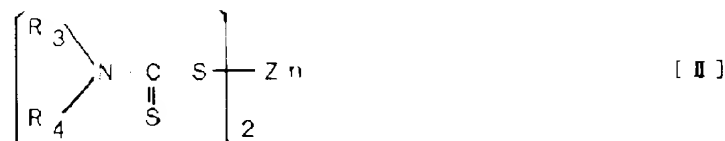


〔ただし、 $R_1$ 、 $R_2$ はそれぞれ独立して炭素数1～18の直鎖アルキル基、分岐鎖アルキル基、環状アルキル基あるいはフェニル基、ベンジル基を示し、更に $R_1$ 、 $R_2$ を連結せしめた炭素数5～8の脂環状基又は一般式〔I〕中に示されている窒素原子以外にヘテロ原子を含む複素環を示す。 $X$ は1～6の整数を示す。〕

[0011]

[Formula 6]

一般式



〔ただし、 $R_3$ 、 $R_4$ はそれぞれ独立して炭素数1～18の直鎖アルキル基、分岐鎖アルキル基、環状アルキル基あるいはフェニル基、ベンジル基を示し、更に $R_3$ 、 $R_4$ を連結せしめた炭素数5～8の脂環状基又は一般式〔II〕中に示されている窒素原子以外にヘテロ原子を含む複素環を示す。〕

[0012]

[Formula 7]



## 一般式



[ただし、 $R_5$ 、 $R_6$  はそれぞれ独立して炭素数 1～8 のアルキル基を、 $n$  は 1 以上の整数を示す。]

[0013] the dialkyl tin oxide 0.1 - the 5.0 weight sections which are expressed with the dithiocarbamic-acid zinc compound 0.1 - the 5.0 weight sections which are expressed with the thiuram compound 0.1 - the 5.0 weight sections, and/or the above-mentioned general formula [II] which are expressed with the above-mentioned general formula [I], and the above-mentioned general formula [III] -- or . [0014]

[Formula 8]

## 一般式



[ただし、 $R_7$ 、 $R_8$  はそれぞれ独立して炭素数 8～18 の直鎖アルキル基、  
分岐鎖アルキル基、環状アルキル基を示す。 $X$  は 1～6 の整数を示す。]

[0015] When the specific thiuram compound 0.1 - the 5.0 weight sections which are expressed with the above-mentioned general formula [IV] are blended, for it to be surprised about a rubber vibration insulator constituent The rubber vibration insulator property of the vulcanized-rubber constituent, especially decline in \*\*\*\*\* are found out, about a low febrility rubber constituent The exoergic improvement effect that it is high when the high exoergic improvement effect applies to styrene-butadiene rubber further is found out without doing a \*\*\*\*\* operation, when it applies to natural rubber and polyisoprene rubber, and it came to complete this invention based on these knowledge.

[0016] The thiuram compound and/or the dithiocarbamic-acid zinc compound, the above-mentioned dialkyl tin oxide, or the above-mentioned specific thiuram compound of this invention is easily added during rubber processing to the constituent for rubber vibration insulators. The feature has little influence and it may raise a rubber vibration insulator property to the processing stability and the vulcanized-rubber physical properties of an unvulcanized rubber Furthermore, there is little influence of the processing stability on an unvulcanized rubber to a low febrility rubber constituent. And it has the feature which it not only demonstrates the low febrility improvement effect, but can demonstrate the low febrility improvement effect to styrene-butadiene rubber etc., without carrying out and doing a 8 solution operation, when it applies to natural rubber and polyisoprene rubber.

[0017] As rubber which makes the subject of the rubber constituent of this invention Polyisoprene rubber (IR) besides natural rubber, styrene-butadiene rubber (SBR), Although various synthetic rubber, such as butadiene rubber (BR), acrylonitrile-butadiene rubber (NBR), isobutylene isoprene rubber (IIR), chloroprene rubber (CR), and ethylene-propylene rubber (EPDM), is illustrated About the constituent for rubber vibration insulators, one or more sorts of blend rubber of the above-mentioned synthetic rubber which made natural rubber or natural rubber the subject further from points, such as vibration isolation nature, about a low febrility rubber constituent It is natural rubber, polyisoprene rubber, styrene-butadiene rubber, butadiene rubber, isobutylene isoprene rubber, etc., and independent or two or more sort combined use is preferably used in these rubber.

[0018] The thiuram compound of the above-mentioned general formula [I] concerning this invention Tetramethylthiurammonosulfide, tetramethylthiuramdisulfide, A tetraethylthiuram disulfide, tetrabutylthiuram disulfide, Tetrapod hexyl thiuram disulfide, tetrapod benzyl thiuram disulfide, Screw (N-ethyl-N-phenyl) thiuram disulfide, tetrakis (2-ethylhexyl) thiuram disulfide, Although tetrapod stearyl thiuram disulfide, dipentamethylenethiuramtetrasulfide, a JIPENTAMETHIUREN thiuram hexa sulfide, tetraeyclo hexyl thiuram disulfide, and dimorpholino thiuram disulfide are mentioned It is not limited to these.

[0019] The dithiocarbamic-acid zinc compound of the above-mentioned general formula [II] concerning this invention A zinc

dimethyldithiocarbamate, a zinc diethyldithiocarbamate, Zinc dibutyldithiocarbamate, N-ethyl-N-phenyl dithiocarbamic-acid zinc, N-pentamethylene dithiocarbamic-acid zinc, dibenzyl dithiocarbamic-acid zinc. Although screw (2-ethylhexyl) dithiocarbamic-acid zinc, dihexyl dithiocarbamic-acid zinc, distearyl dithiocarbamic-acid zinc, dicyclohexyl dithiocarbamic-acid zinc, and morpholino dithiocarbamic-acid zinc are mentioned, it is not limited to these. An above-mentioned thiuram compound and an above-mentioned dithiocarbamic-acid zinc compound can be adjusted by the well-known method.

[0020] A monomer type ( $n=1$ ) or polymer types ( $n\geq 2$ ), such as dimethyl tin oxide, di-n-butyl tin oxide, and G n-octyl tin oxide, are mentioned, and, as for the dialkyl tin oxide of the above-mentioned general formula [III] concerning this invention, especially the monomer type or polymer type of di-n-butyl tin oxide and G n-octyl tin oxide has commercial usable elegance. The specific thiuram compound of the above-mentioned general formula [IV] concerning this invention is not limited to these, although tetrakis (2-ethylhexyl) thiuram disulfide and tetrapod stearyl thiuram disulfide are mentioned. This kind of specific thiuram compound can also be adjusted by the well-known method.

[0021] The loadings to the rubber 100 weight section of the above-mentioned thiuram compound concerning this invention and a dithiocarbamic-acid zinc compound are the 0.1 - 5.0 weight section, and in order that vulcanization speed may become quick in the amount which there are almost no target vibrationproofing effect and target exoergic improvement effect, and exceeds the loadings and they may worsen the processing stability of an unvulcanized-rubber constituent remarkably, they are difficult to use it at under the loadings. However, the vibrationproofing effect and especially the exoergic improvement effect are demonstrated by the combined use with specific thiuram compound independent use or a thiuram compound and/or a dithiocarbamic-acid zinc compound, and dialkyl tin oxide.

[0022] The loadings to the rubber 100 weight section of the above-mentioned specific thiuram compound concerning this invention are the 0.1 - 5.0 weight section, and in order that vulcanization speed may become quick in the amount which there are almost no target vibrationproofing effect and target exoergic improvement effect, and exceeds the loadings and they may worsen the processing stability of an unvulcanized-rubber constituent remarkably, they are difficult to use it at under the loadings. The loadings to the rubber 100 weight section of the dialkyl tin oxide concerning this invention are the 0.1 - 5.0 weight section, in the amount which there are almost no target vibrationproofing effect and target exoergic improvement effect, and exceeds the loadings, they make vulcanization speed late and it becomes difficult to vulcanization speed adjust them under at the loadings.

[0023] The above-mentioned thiuram compound (a specific thiuram compound is also included,) and above-mentioned dithiocarbamic-acid zinc compound concerning this invention are usually used as the vulcanization accelerator for rubber, or agricultural chemicals. Although it is an example, it is reported to [Society of Rubber Industry, Japan, volume [ 45th ] No. 8, and 745 (1972)] that tetrakis (2-ethylhexyl) thiuram disulfide has an effect as a vulcanization accelerator for rubber. However, the indication about improving the damping characteristic of a rubber constituent and febrility is not yet found out like this invention by adding these thiuram compounds and/or a dithiocarbamic-acid zinc compound, dialkyl tin oxide, or a specific thiuram compound.

[0024] Although what has been used conventionally can use the compounding agent blended with the rubber constituent concerning this invention as it is. When it illustrates, metallic oxides, such as fatty acids, such as stearin acid, a zinc oxide, and a magnesium oxide. Vulcanizing agents, such as sulfur, a thiazole system, a sulfenamide system, a thiuram system. Vulcanization accelerators, such as a dithiocarbamic-acid salt system and a thiourea system, an amine system. Antioxidants, such as a phenol system, an imidazole system and a dithiocarbamic-acid metal salt, and a wax. It shall also be included by the claim of this invention that compounding agents for rubber, such as a bulking agent of softeners, such as straight mineral oil, carbon black, and an inorganic system, a reinforcing agent, and a tackifier, may be suitably blended according to the purpose. It is a book below.

[ Translation done ]

## \*NOTICES\*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1 This document has been translated by computer. So the translation may not reflect the original precisely.
- 2 \*\*\*\* shows the word which can not be translated.
- 3 In the drawings, any words are not translated.

## EXAMPLE

[Example]

Based on combination of examples 1-15, the example 1 of comparison - 10, table 1, the thiuram compound or dithiocarbamic-acid zinc compound based on the loadings of rubber, a zinc oxide, stearin acid, carbon black, and Table 2 by 75 cc Banbury mixer [Oriental Energy Machine factory lab plastic strike mill], dialkyl tin oxide, or the thiuram compound (a specific thiuram compound is included) was kneaded for 4 minutes with the rotational speed of 70rpm. The rubber temperature at the time of the milling going up was 140-150 degrees C. Subsequently, based on Table 1, a vulcanization accelerator and sulfur are kneaded for this kneading object with the test roll of 50-60 degrees C of roll skin temperatures, and it is JIS about this unvulcanized-rubber constituent after that. K Based on 6300-1994 (the unvulcanized-rubber physical-test method die vulcanization examination A method), the curelast meter examination [150 degrees C, amplitude angle: \*\*3 degree] was performed. Furthermore, press cure is carried out on the vulcanization conditions which show this unvulcanized-rubber constituent in Table 2, a vulcanized-rubber constituent is produced, this vulcanized-rubber constituent is used, and it is JIS. Ordinary state physical properties are measured based on K6301 (the vulcanized-rubber physical-test method), and it is JISK further. Based on 6254 (the stress and strain test method in low deformation of vulcanized rubber), the static modulus (G25) was measured at 23 degrees C. Furthermore, a dynamic modulus (E') and tandelta were measured at 23 degrees C by Oriental Energy Machine factory LEO log rough solid. However, \*\*\*\*\* was computed by  $(100\text{Hz } E')/(1\text{Hz } E')$ . Those results were shown in Table 2.

[0026]

[Table 1]

表

1

天然ゴム	100
酸化亜鉛	5
ステアリン酸	1
FEFカーボンブラック	40
硫黄	2
加硫促進剤 (*1) ノクセラー CZ)	1
供試試料	[表2に記載]

\*1) ノクセラー CZ : N-シクロヘキシル-2-

ベンゾチアゾリルスルフェンアミドの大内新興

化学工業株式会社商品名。

[0027]

[Table 2]

表 2 (その1)

		実 施 例									
		1	2	3	4	5	6	7	8	9	10
供試 試料	*2) TR・DC	*4) TST	*5) TOT	*6) THT	*7) TBT	*8) TET	*9) TT	*10) TS	*11) TBZT	*12) TPET	*13) BZ
	配合量 [PHR]	2.38	1.28	1.04	0.82	0.21	0.17	0.15	1.09	0.78	0.95
	*3) 顔化合物	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)	BT0 (P)
	配合量 [PHR]	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
キュラスト メータ試験 (150℃)	t'c(10) [min]	2.3	3.4	3.2	3.2	2.5	2.0	2.6	2.3	4.0	2.0
加硫時間 [min]	150℃	10	10	10	15	10	10	10	10	10	10
引張試験 (常態物性)	M200 [MPa]	9.9	10.4	11.1	9.9	11.9	11.8	10.5	11.5	11.5	10.6
防振特性	G25 [MPa]	1.31	1.27	1.30	1.26	1.41	1.40	1.35	1.36	1.38	1.28
	動伝率	1.040	1.045	1.065	1.063	1.054	1.050	1.052	1.059	1.047	1.060
	tan δ [20Hz]	0.0610	0.0695	0.0677	0.0699	0.0720	0.0659	0.0689	0.0758	0.0758	0.0698
	100Hz [MPa]	3.854	3.955	4.173	3.583	3.745	4.306	4.345	4.308	4.338	4.320
	1Hz [MPa]	3.706	3.785	3.918	3.371	3.554	4.101	4.130	4.068	4.142	4.078

\*2) TR・DC : チウラム化合物 (特定チウラム化合物を含む。) 及びジチオカルバミン酸亜鉛化合物。

\*3) 顔化合物 : BT0 (P) ; ジブチル銅オキシド (ポリマータイプ) , BT0 (H) ; ジブチル銅オキシド (モノマータイプ) ,  
OT0 (P) ; ジオクチル銅オキシド (ポリマータイプ)

表 2 (その2)

		実 施 例					比 較 例				
		11	12	13	14	15	1	2	3	4	5
供試 試料	*2) TR・DC	*14) ZP	*5) TOT	*5) TOT	*4) TST	*5) TOT	*6) THT	*7) TBT	*8) TET	*9) TT	*10) TS
	配合量 [PHR]	1.22	1.26	1.20	2.38	1.26	1.04	0.82	0.21	0.17	0.15
	*3) 顔化合物	BT0 (P)	BT0 (H)	OT0 (P)	—	—	—	—	—	—	—
	配合量 [PHR]	0.99	0.99	0.99	—	—	—	—	—	—	—
キュラスト メータ試験 (150℃)	t'c(10) [min]	1.7	3.5	3.9	2.3	2.9	2.7	2.3	2.2	1.8	2.8
加硫時間 [min]	150℃	10	10	10	10	10	10	10	10	10	10
引張試験 (常態物性)	M200 [MPa]	10.3	10.5	11.3	10.6	12.3	12.5	13.3	12.5	12.9	12.7
防振特性	G25 [MPa]	1.34	1.29	1.32	1.32	1.38	1.49	1.50	1.48	1.50	1.58
	動伝率	1.050	1.045	1.053	1.045	1.048	1.078	1.074	1.068	1.063	1.078
	tan δ [20Hz]	0.0577	0.0691	0.0703	0.0694	0.0723	0.0709	0.0678	0.0673	0.0527	0.0768
	100Hz [MPa]	3.953	3.960	4.103	4.178	4.454	4.664	4.763	4.653	4.544	5.070
	1Hz [MPa]	3.765	3.786	3.900	3.998	4.252	4.333	4.438	4.356	4.276	5.017

表 2 (その3)

		比較例				
		6	7	8	9	10
供試 試料	*2) TR・DC	*11) TBzT	*12) TPtT	*13) BZ	*14) ZP	—
	配合量 [PHR]	1.09	0.78	0.95	1.22	—
	*3) 銅化合物	—	—	—	—	—
	配合量 [PHR]	—	—	—	—	—
キュラスト メータ試験 (150℃)	T <sub>c</sub> (10) [min]	1.8	3.6	2.1	1.6	4.3
加硫時間 [min] 150℃		10	10	10	10	15
引張試験 (常態物性)	M200 [MPa]	12.9	11.8	12.6	12.6	12.9
防振特性	G25 [MPa]	1.59	1.49	1.52	1.54	1.43
	動倍率	1.063	1.079	1.072	1.060	1.074
	tan δ [20Hz]	0.0527	0.0780	0.0725	0.0610	0.0741
	100Hz [MPa]	4.544	4.944	4.796	4.884	4.814
	1Hz [MPa]	4.276	4.581	4.475	4.609	4.482

- \*4) ISI : テトラステアリルチウラムジスルフィド    \*5) TOT : テトリス (2-エチルヘキシル) チウラムジスルフィド  
 \*6) THT : テトラヘキシルチウラムジスルフィド    \*7) TBT : テトラブチルチウラムジスルフィド  
 \*8) TET : テトラエチルチウラムジスルフィド    \*9) TT : テトラメチルチウラムジスルフィド  
 \*10) TS : テトラメチルチウラムモノスルフィド    \*11) TBzT : テトラベンジルチウラムジスルフィド  
 \*12) TPtT : ビス (N-エチル-N-フェニル) チウラムジスルフィド    \*13) BZ : ジブチルジチオカルバミン酸亜鉛  
 \*14) ZP : N-ペンタメチレンジチオカルバミン酸亜鉛

[Translation done]